

**ANALYSIS OF THE TEMPORAL EVOLUTION OF THERMAL
CONDUCTIVITY IN ALUMINA–WATER NANOFLUID**

A Senior Scholars Thesis

by

STEPHEN DALE FORTENBERRY, JR.

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2008

Major: Nuclear Engineering

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Approved by:

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ABSTRACT

Analysis of the Temporal Evolution of Thermal Conductivity in Alumina–Water Nanofluid (April 2008)

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In this effort, the temporal behavior of a manufactured alumina (Al_2O_3) – water nanofluid was evaluated. Measurements of nanofluid effective thermal conductivity were acquired over an extended time period. Analysis of acquired measurements elucidated the degradation of nanofluid effective thermal conductivity with respect to time. Specifically, the measured thermal conductivity of nanofluid decreased from an initial value of $0.6365 \text{ W/m-}^\circ\text{C}$ to a final value of $0.6130 \text{ W/m-}^\circ\text{C}$ over a period of several months. This corresponded to a change in the thermal conductivity enhancement realized due to the suspension of nanoparticles in fluid from an initial value of 11.2% to a final value of 7.2%. Temporal evolution of the nanofluid's thermal conductivity is attributed to changes in the stability of the colloidal suspension. Future work is planned to investigate the physical mechanisms controlling this phenomenon.

DEDICATION

To my mother (*Becky*) and father (*Steve*)

ACKNOWLEDGMENTS

I would like to acknowledge Elvis Efren Dominguez-Ontiervos. He has been an exceptional mentor and friend throughout the time I have worked in Dr. Hassan's Multi-phase Research Laboratory (MPRL), and I am very thankful for his guidance throughout my pursuit of research efforts, including my investigations of the temporal evolution of nanofluid.

I would also like to acknowledge Dr. Yassin Hassan for his support of my research efforts. It has been a privilege to conduct research for Dr. Hassan. I especially appreciate his recognition of my efforts in technical publications and the trust he has demonstrated by allowing me to represent him at national conferences through the presentation of his group's research to the engineering community.

It should also be noted that the research of nanofluids was supported by grants from both the United States Department of Energy and Texas Advanced Research Program.

NOMENCLATURE

D	Thermal diffusivity
Ei	Exponential integral
k	Thermal conductivity
k_n	Nanofluid thermal conductivity
k_b	Base fluid thermal conductivity
Δk	Enhancement of fluid thermal conductivity (due to dispersion of nanoparticles)
Q	Quantity of heat (applied instantaneously)
q	Rate of heat dissipation
r	Distance from the heat source
r^2	Calculated residual value
t	Time elapsed after the initiation of heating (either transient or instantaneous)
t_l	Heating time (transient heating applications)
u_k	Intrinsic (relative) uncertainty of KD2 Pro thermal conductivity measurements
u_{k_n}	Calculated (relative) uncertainty of measured values for nanofluid thermal conductivity
$u_{\Delta k}$	Calculated (relative) uncertainty of measured values for the enhancement of fluid thermal conductivity

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CHAPTER I

INTRODUCTION

Nanofluids – colloidal suspensions of nano-size (<100 nm) particles in conventional heat transfer fluid – are among the many innovations resulting from the advent of nanotechnology. These novel heat transfer fluids were first investigated by Masuda et al. [1] and Choi [2] in the previous decade. Since their development, numerous inquiries investigating nanofluids have been conducted to compare the properties of these dispersions to conventional heat transfer fluids. Through these inquiries, experimenters have noted significant differences in colloidal suspensions of nanoparticles, relative to previously investigated suspensions of milli- or micro-sized particles [3].

Among the properties investigated is that of nanofluid thermal conductivity. In previous investigations researchers have noted that fluids' thermal conductivity is generally enhanced, relative to that of conventional heat transfer fluids, when nanoparticles are suspended in the fluid. These observations are of importance because the enhancement of a fluids' thermal conductivity would be expected to improve the heat transfer capabilities of the fluid. Such enhancements are significant due to the burgeoning demands placed upon heat transfer systems by developing technologies. Numerous

This thesis follows the style of the International Journal of Heat and Mass Transfer.

theories regarding the physical phenomena contributing to this enhancement have been proposed. However, such assertions have been widely debated in the heat transfer and material science community and, to date, no single theory has gained wide acceptance. As previously noted, fluid properties are modified due to the suspension of solid particles in conventional heat transfer fluid. It should be noted that one would not expect particles to suspend indefinitely in a fluid. Additionally, the properties of a nanofluid would be expected to vary as a function of the suspension of nanoparticles in the fluid. Thus, the colloidal stability of nanoparticle suspensions is also relevant to investigations of nanofluid behavior.

In this effort, the temporal behavior of a manufactured alumina (Al_2O_3)-water nanofluid was evaluated. Measurements of nanofluid effective thermal conductivity were acquired over a period of several months. Analysis of acquired measurements elucidated the degradation of nanofluid effective thermal conductivity with respect to time. The temporal evolution of the nanofluid's thermal conductivity is attributed to changes in the stability of the colloidal suspension and future work is planned to investigate the physical mechanisms controlling this phenomenon.

Thermal conductivity enhancement of nanofluids

As previously noted, suspensions of nanoparticles in conventional heat transfer fluids were first investigated by Masuda et al. [1] and Choi [2] in the previous decade. Each of these investigations involved evaluation of the fluids' thermal

conductivity. Since these initial inquiries numerous investigations of the enhancement of thermal conductivity, due to the suspension of nanoparticles in conventional heat transfer fluids, have been conducted. While a complete summary of all relevant experimental investigations is beyond the scope of the present work, a review of several relevant works is in order. The work of Trisaksri and Wongwises [4] is recommended as review of previous studies of nanofluid behavior.

Most frequently, studies of nanofluids' thermal conductivity involve the investigation of dispersions of oxide nanoparticles in either ethylene glycol or water. In the work of Kim et al. [5], the authors describe investigations of the thermal conductivity of dispersions of nanoparticles of several compositions – alumina (Al_2O_3), zinc-oxide (ZnO), and titanium dioxide (TiO_2) – in both water and ethylene glycol utilizing the transient hot-wire method. In this study, the size of the nanoparticles suspended and the nanoparticle concentration in the dispersion developed were varied in an effort to analyze the effects of these parameters upon nanofluid thermal conductivity. Experimenters observed that nanofluid thermal conductivity increased as particles size decreased consistently in tests involving various combinations of base fluid and nanoparticle composition. These observations allowed the authors' to assert that nanofluid thermal conductivity would, all other properties being equal, be expected to be greater for dispersions of smaller nanoparticles.

Eastman et al. [3] reported observations of the thermal conductivity of nanofluids containing metallic nanoparticles. Specifically, copper nanoparticles were dispersed in ethylene glycol. Researchers noted that the thermal conductivity enhancement observed for nanofluids involving the dispersion of metallic nanoparticles was significantly greater, relative to those involving the dispersion of oxide nanoparticles.

In addition to experimental observations, theoretical postulations have been made regarding the enhancement of fluid thermal conductivity due to the introduction of nanoparticles. Such theoretical assertions are of great interest due to the inability of established theories to adequately quantify observed enhancements [6]. In a recent work, Jang and Choi [6] asserted that observed enhancements may be a result of nano-scale convection due to Brownian motion effects. However, other works have asserted that Brownian motion effects have relatively little influence upon nanofluid thermal conductivity [7]. Theorists have also postulated that nanoparticles suspended in fluid may be modeled as particles possessing interfacial shells [8] or nanolayers composed of interfacial particles [9] in an effort to explain observed enhancements of fluid thermal conductivity. Fractal models have also been proposed to describe the effect of nanoparticles suspensions upon fluid thermal conductivity [10]. However, to date no theory regarding the mechanisms controlling the enhancement of fluid thermal conductivity or correlation to adequately predict observed thermal conductivity enhancements has been agreed upon.

Nanofluid colloidal stability

As previously asserted, the colloidal stability of nanoparticle suspensions is relevant to investigations of nanofluid behavior. This particular aspect is of significance because nanofluids are suspensions of solid particles in conventional heat transfer fluids. Thus, the properties of nanofluids are expected to vary as functions of the suspension of nanoparticles established in the fluid. One such phenomenon affecting the stability of nanofluids is the agglomeration of nanoparticles in a developed suspension.

Agglomeration results in the formation of larger particles in the fluid and may ultimately reduce the number of nanoparticles suspended in a fluid.

Williams [11] provides a detailed description of mechanisms controlling the stability of colloidal suspensions of nanoparticles in fluid. In this work, Williams asserts that the importance of surface effects for particles approximately 100 nm in size is much greater than that of surface effects in “bulk material.” Williams also discusses the use of surfactants and dispersants, or control of fluid pH, to maintain surface energies that support of the suspension of nanoparticles in fluid. Understanding these physical mechanisms is critical to the development of an appreciation of the behavior of nanoparticles suspended in fluid.

The processes described in Williams [11] are frequently utilized due to their ability to prevent agglomeration, and therefore maintain the colloidal stability, of particles in the base fluid. In experiments of Kim et al. [5], surfactant was added to prevent rapid

settling of particles from the suspension. The authors noted that the settling affect was undesirable since the rapid removal of particles from suspension would also cause the rapid degradation of fluid thermal conductivity.

However, interest in the colloidal stability of nanofluids extends beyond concerns of particles settling out of suspension. The work of Yoo et al. [12] reports experimental investigations of the effect of base fluid pH upon fluid thermal conductivity for Al_2O_3 nanofluids. In this investigation, nanofluid thermal conductivity was observed to vary as a function of base fluid pH. Specifically, it was reported that nanofluid with a pH deviating most significantly from that of a neutral fluid possessed the highest thermal conductivity, relative to other fluids tested. This observation supported the author's assertion that the pH of fluids may be adjusted in order to improve the thermal conductivity enhancement of nanofluids. It is postulated that the variation of fluid pH affects the agglomeration of nanoparticles in fluid by counteracting van der Waals forces, which promote the agglomeration of nanoparticles. However, Yoo et al. asserts that the adjustment of fluid pH to prevent particle agglomeration improves nanofluid thermal conductivity by maximizing the surface-to-volume ratio of particles suspended in the fluid. This supports assertions that a fluid's thermal conductivity is not only affected by particles settling out of suspension but also by increasing the effective size of particles suspended in the fluid. Such an assertion is also corroborated by the observations of Kim et al. [5] which noted that nanofluid thermal conductivity decreased as particle size increased.

CHAPTER II

METHODS

The nanofluid investigated in this effort was developed by the NEI Corporation through the suspension of NanomyteTM alumina (Al_2O_3) nanoparticles in water. The manufacturer specified the particle concentration as 15 wt.% (4.45 vol%). The pH of the water, which served as the base fluid for this suspension, was adjusted such that the nanofluid possessed a pH between 3 and 4. This measure enhanced the stability of the colloid suspension without the use of dispersants or surfactants. Individual particles were characterized as ranging between 50 nm and 100 nm in size. However, the manufacturer also specified that agglomerations on the order of 200 nm were to be expected. Prior to the execution of the experiment, the nanofluid investigated was sonicated for approximately two hours using a bath-type sonifier (Branson 1510). This measure was taken to reduce the agglomeration of particles and enhance the stability of the colloidal suspension of nanoparticles in fluid.

Following sonication, the nanofluid was placed in a single 250 mL beaker. A probe was inserted into nanofluid to allow acquisition of thermal conductivity data via the KD2 Pro Thermal Properties Analyzer (Decagon Devices). For this investigation, the KS-1 probe (Decagon Devices) was selected due to its superior measurement capabilities – individual measurements of thermal conductivity were accurate to within 5% of the true value of the quantity [13]. A representation of the experimental setup implemented to

provide appropriate conditions for characterizations of the nanofluid's thermal conductivity over extended time periods is presented in Figure 1.

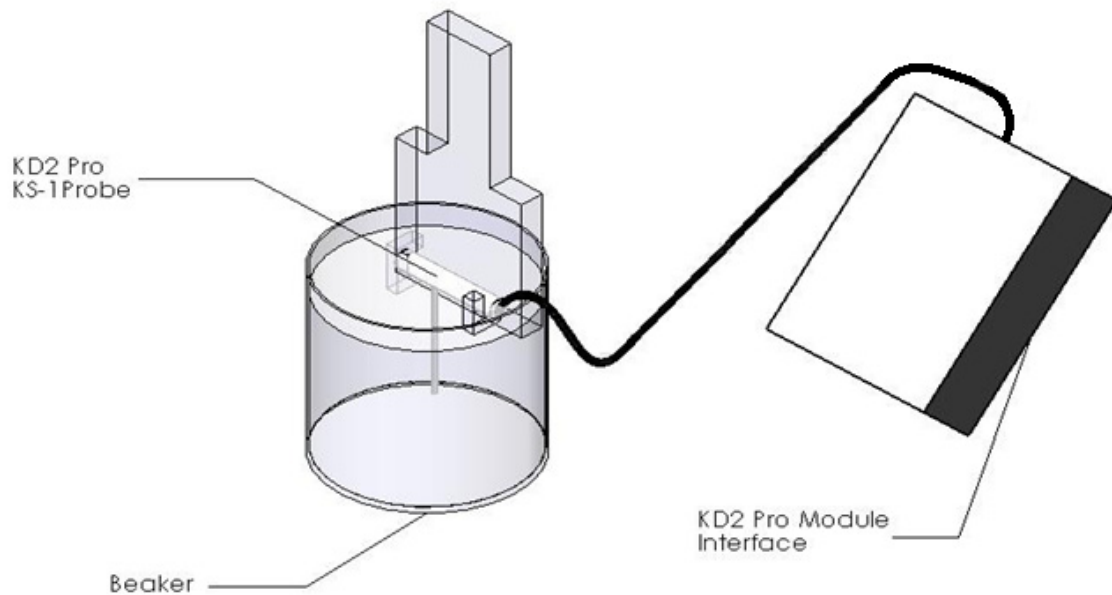


Figure 1. Schematic of thermal conductivity measurement apparatus [14]

The basis for the model implemented by the KD2 Pro to measure the thermal properties of materials is detailed in the manual accompanying the device [13]. However, an understanding of the model implemented, and the analytical schemes utilized, by the manufacturer to measure the thermal conductivity of materials is of significance and allows an appreciation of the physical phenomena modeled. Thus an overview of this model is provided as an Appendix to this work.

It should be noted that certain efforts were made, in accordance with the recommendations provided by the device manufacturer in the work of Cobos [15], to ensure the accuracy of experimental measurements. Such efforts were essential to the prevention of heat transfer by either forced convection or free convection of the fluid, and allow accurate the measurement of fluid thermal conductivity.

Efforts were made to prevent unnecessary disturbances of the fluid during daily operations in the laboratory which would result in forced convection of the fluid. For the measurements presented in the following results section, the probe was not removed at any time from the fluid volume and is assumed to remain in a fixed position throughout the measurement of nanofluid thermal conductivity. This measure was implemented to reduce observed fluctuations in initial measurements of thermal conductivity during which time the probe was removed for cleaning and re-inserted into the fluid. Such practice was appropriate both to reduce forced convection of the fluid and because disturbances would also be expected to enhance the colloidal stability of the suspension – an undesirable effect in the present work which sought to analyze of the temporal evolution of a stagnant alumina-water nanofluid.

In an effort to prevent free convection of the fluid, insulation was employed both below and around the measurement volume in the physical implementation of this system. This measure was undertaken to reduce free convection of the fluid due to variations in laboratory ambient temperature.

It should also be noted that the measurement probe was oriented vertically in the fluid.

This orientation was that recommended in the work of Cobos [15] because it effectively reduces free convection of the fluid during the heating of the measurement probe. Cobos recommended the vertical orientation, rather than the horizontal orientation, of the probe because the contribution of free convection to the transfer of heat in a fluid is inversely proportional to the characteristic dimension of the heat source. In this work, it was noted that the characteristic dimension of a vertically oriented probe is represented as its length and that of a horizontally oriented probe is its diameter. Thus, since the length of the probe implemented is significantly greater than the diameter of the probe, Cobos recommends that the probe be oriented vertically to minimize free convection of the fluid.

It should also be noted that initial measurements of nanofluid thermal conductivity were conducted at relatively short time intervals of 15 min. However, this procedure proved to create fluctuations in experimental measurements due to the frequent heating of the fluid by the probe. Therefore measurement frequency was decreased so that data was acquired at a 12 hour time intervals. This technique provided the time resolution required while ensuring the nanofluid investigated remained stagnant throughout the execution of the experiment.

To allow the thermal conductivity enhancement observed for nanofluid to be attributed to the suspension of nanoparticles in the fluid, rather than another effect (i.e the

adjustment of fluid pH), the thermal conductivity of the base fluid –the fluid in which the nanoparticles were dispersed – was also measured. A sample of the base fluid utilized in the development of the nanofluid investigated was provided by NEI Corporation. This fluid was assumed to be identical to the nanofluid investigated, with the exception that no particles had been suspended in this sample. The thermal conductivity of this fluid was measured to allow comparison of this quantity with measurements of nanofluid thermal conductivity. Such a comparison allowed differences observed between the thermal conductivity of the nanofluid and that of the base fluid to be attributed only to the dispersion of nanoparticles in the fluid. It should also be noted that the thermal conductivity of the base fluid was assumed to be constant over time.

CHAPTER III

RESULTS

Data processing scheme

A discussion of the data processing methods utilized in the development of experimental results is first in order. As previously noted, thermal conductivity measurements were, generally, conducted once every 12 hour period. However, these intervals were not strictly maintained through the conduction of the experiment. Such realities necessitated development of an approach to determine representative values for all quantities measured during the conduction of the experiment. Thus, thermal conductivity measurements conducted within the period of a day were averaged to provide a value representative of the nanofluid thermal conductivity for that particular day. For all measurements presented in this work, averages were developed from two daily measurements to provide consistency in quantifications of the uncertainties inherent to all measurements reported.

The enhancement of fluid thermal conductivity due to the suspension of nanoparticles, relative to that of the base fluid, was determined through comparison of the measured nanofluid conductivity to that of the base fluid tested. The calculation of this relative enhancement (Δk) was accomplished through the implementation of Equation 1, where k_n represents a single daily (averaged) thermal conductivity value of the nanofluid and k_b the measured thermal conductivity of the base fluid. It should be noted that only a single

measurement of base fluid thermal conductivity was utilized in the calculation of the base fluid thermal conductivity.

$$\Delta k = \frac{k_n - k_b}{k_b} \quad (1)$$

It should be noted that measurements conducted prior to the institution of acceptable experimental methods – initial measurements conducted at relatively short time intervals and prior to the termination of efforts to clean the probe – were discarded. Also, data which did not compare well with the mathematical model implemented by the KD2 Pro to determine fluid thermal conductivity (i.e. $r^2 < 1.0000$) was discarded.

Since data was acquired at different times of day and over the period of several months it would be expected that temperature, a parameter controlling materials' thermal conductivity, would not remain constant throughout the study period. The dependence of nanofluid thermal conductivity upon temperature was noted for measurements conducted. Therefore a temperature range over which nanofluid thermal conductivity demonstrated relatively little dependence upon temperature was selected to allow proper analysis of the temporal evolution of nanofluid thermal conductivity. It should also be noted that measurement of the base fluid thermal conductivity was conducted under conditions such that the base fluid temperature was within the temperature range selected for evaluation of nanofluid thermal conductivity.

Observed temporal evolution of nanofluid thermal conductivity

Processed experimental data is presented in Figures 2 and 3. Figure 2 depicts the evolution of nanofluid thermal conductivity (k_n) with respect to time. It should be emphasized that the time basis for experimental measurements was established as the time at which significant oscillations of measured nanofluid thermal conductivity, which were attributed to the inadequacy of experimental conditions, were observed to decrease. This figure demonstrates that the measured thermal conductivity of the nanofluid decreased over the time period of experimental measurements. Specifically, the nanofluid thermal conductivity was observed to decrease from an initial value of 0.6365 W/m-°C to a final value of 0.6130 W/m-°C.

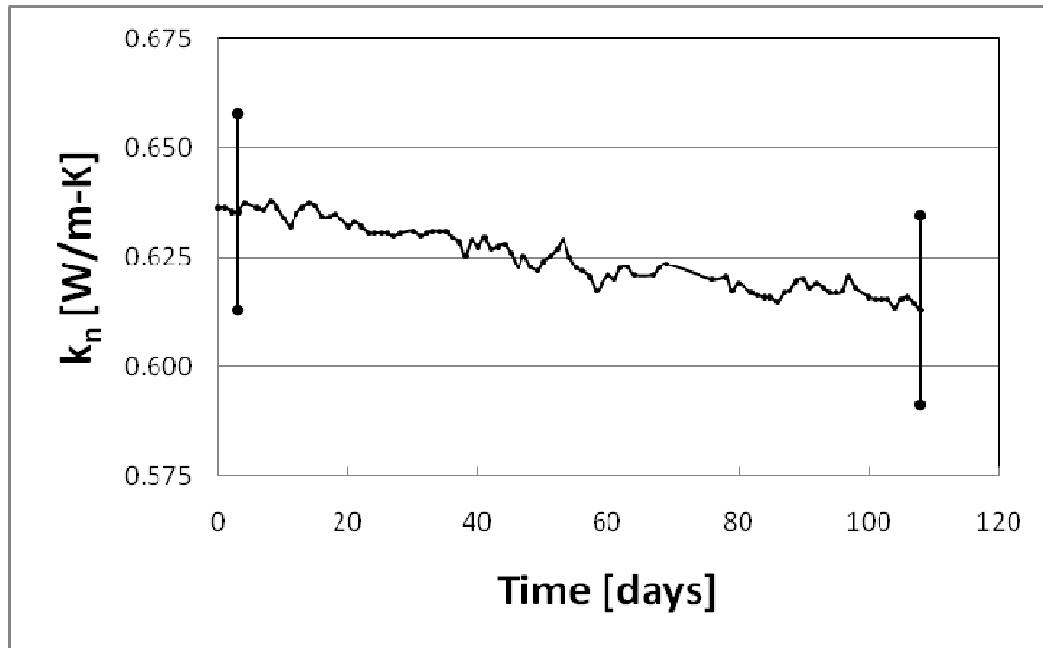


Figure 2. Temporal evolution of nanofluid effective thermal conductivity

Figure 3 provides a representation of the temporal evolution of the enhancement of fluid thermal conductivity due to the suspension of nanoparticles (Δk). Such analysis is of importance since it is observations of the enhancement of nanofluids' thermal properties, relative to those of conventional heat transfer fluids, which drives investigations of these fluids. For measurements acquired in this investigation, an initial enhancement of fluid thermal conductivity of 11.2% was calculated. During the execution of the investigation, the measured enhancement degraded to a final value of 7.2%.

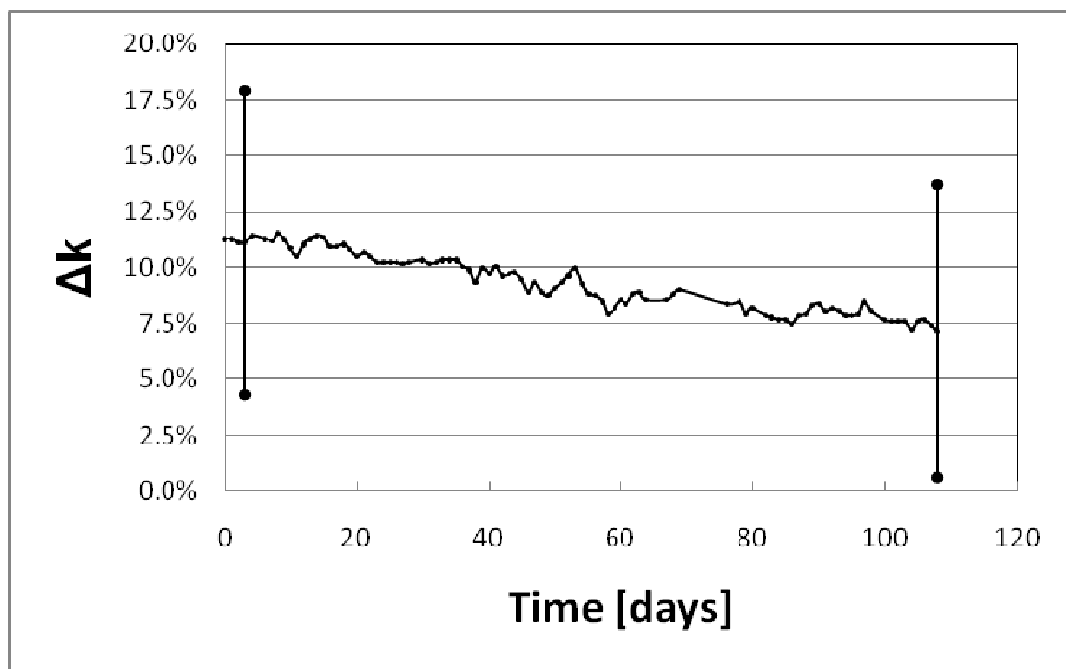


Figure 3. Temporal evolution of nanofluid thermal conductivity enhancement

Uncertainty analysis of experimental measurements

In the quantitative analysis of uncertainties associated with experimental measurements, only the error associated the KD2 Pro Thermal Properties Analyzer was taken into account. The error bars depicted in Figures 2 and 3 demonstrate representative values for the uncertainty expected in evaluations of nanofluid thermal conductivity (k_n) and the enhancement of fluid thermal conductivity due to the suspension of nanoparticles (Δk). Mathematical relationships for the quantification of uncertainties were developed utilizing the analysis methodology detailed in Fox et al. [16]. Equation 2 provides the mathematical relationship implemented to calculate representative values for the relative uncertainty present in quantifications of nanofluid thermal conductivity (u_{k_n}). In this equation u_k represents the uncertainty of individual measurements of fluid thermal conductivity ($u_k = \pm 5.0\%$) and k_n represents the calculated averaged thermal conductivity. The measured values for thermal conductivity, from which the average thermal conductivity was calculated, are represented by $k_{n,1}$ and $k_{n,2}$.

$$u_{k_n} = \frac{u_k}{2k_n} [k_{n,1}^2 + k_{n,2}^2]^{1/2} \quad (2)$$

The uncertainty associated with calculated values of the fluid enhancement due to the suspension of nanoparticles ($u_{\Delta k}$) was determined through the implementation of Equation 3. In this equation, Δk represents the calculated value of the fluid enhancement due to the suspension of nanoparticles and k_b represents the measured thermal conductivity of the base fluid.

$$u_{\Delta k} = \frac{k_n}{\Delta k k_b} [u_k^2 + u_{k_n}^2]^{1/2} \quad (3)$$

It is also recognized that several other factors, which were not taken into account in the preceding quantitative analyses of experimental uncertainties may have also contributed to uncertainties in experimental investigations. Specifically, these factors are identified as: variation of fluid temperature, convective heat transfer in the fluid volume, development of nanoparticle agglomerations upon the measurement probe, and the development of a concentration gradient in the measurement volume. Each of these factors will be treated separately in the following discussion.

The first factor to be discussed, which was not taken into account in the quantitative analysis of experimental uncertainties, is that of the variation of fluid temperature over the time of investigations. In general, thermal conductivity is expected to vary as a function of temperature. However, the effect of temperature upon measurements was limited through the analysis of thermal conductivity measurements over a narrow temperature range (23.05 °C – 24.2 °C) in which nanofluid thermal conductivity demonstrated relatively little dependence upon temperature. A plot of this relationship is provided in Figure 4. This plot reveals that, for the analysis conducted, thermal conductivity was generally independent of temperature. Such knowledge enhances confidence in the validity of the experimental inquiry.

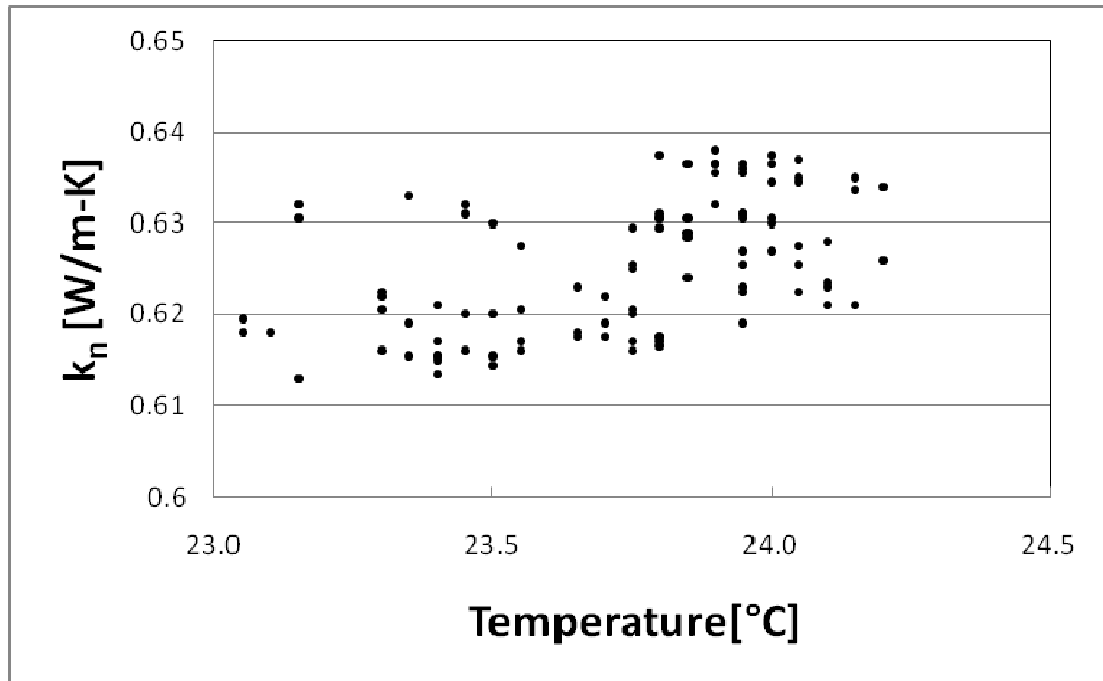


Figure 4. Plot of dependence of nanofluid thermal conductivity upon temperature

The possibility of convective heat transfer in the measurement volume was another potential source of uncertainty in the experiment. However, this potential for convection in the fluid volume was reduced through the prevention of unnecessary disturbances of the fluid. Specifically, the measures undertaken to mitigate the potential for convection of the fluid were the fixing of the probe position, application of insulation materials, and orientation of the probe vertically in the fluid. It should also be noted that convective heat transfer during measurements would be expected to be demonstrated through poor comparisons between experimental temperature measurements and the model implemented for heat conduction [17]. Thus, since only thermal conductivity measurements in which measured data compared well with the theoretical model

implemented (i.e. $r^2 < 1.0000$), it is asserted that the contribution of convective heat transfer to experimental uncertainties were appropriately mitigated in the present investigation.

It is also recognized that the agglomeration of nanoparticles upon the measurement probe may be a source of uncertainty in the current investigation. This uncertainty could have been mitigated through regular cleaning of the probe surface. However, avoidance of convective effects required the probe to remain fixed in the fluid volume and not be removed. It was also desirable to ensure the fluid remained stagnant throughout the conduction of the experiment. Thus, this uncertainty was accepted in order to allow the mitigation of uncertainties expected to result from the unavoidable convection of the fluid during efforts to clean the probe.

The final source of uncertainty to be discussed is that uncertainty attributed to the development of a nanoparticle concentration gradient in the measurement volume. This gradient would be expected to develop as particles settle out of the fluid due to gravitational effects. The impact of this developed nanoparticle concentration gradient was exacerbated by the vertical orientation of the probe and the measured nanofluid thermal conductivity was an average value related to the gradient established along the length of the probe. However, since the probe did not extend the entire length of the beaker and nanoparticles ultimately concentrated in the lowest regions of the fluid volume, this average value measured by the probe would be expected to change. Thus,

measurements of the average nanofluid thermal conductivity in the volume surrounding the probe were accepted due to the desire to mitigate convective heat transfer in the fluid volume.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Summary

In this effort, the temporal behavior of a manufactured alumina-water nanofluid was evaluated. Specifically, measurements of nanofluid effective thermal conductivity were acquired over an extended time period. Analysis of acquired measurements elucidated the degradation of nanofluid effective thermal conductivity with respect to time.

Specifically, it was noted that the thermal conductivity of the nanofluid decreased from an initial value of $0.6365 \text{ W/m-}^{\circ}\text{C}$ to a final value of $0.6130 \text{ W/m-}^{\circ}\text{C}$. This corresponded to a change in the thermal conductivity enhancement realized due to the suspension of nanoparticles in fluid from an initial value of 11.2% to a final value of 7.2%.

Conclusions

The degradation of nanofluid thermal conductivity with respect to time, observed in the execution of the experiment discussed, is attributed to the degradation of nanofluid colloidal stability during the time of the experiment. It would be expected that nanofluid thermal conductivity would decrease as particles are removed from suspension. This assertion that particles settled out of the developed suspension is supported by observations, following experimental measurements, of a substantial nanoparticle layer deposited at the bottom of the beaker utilized in this experiment.

It is also noted that the agglomeration of particles may have resulted in an effective increase in particle size. While this change was not directly observed in the execution of the current experiment, the relationship between the agglomeration of nanoparticles and nanofluid thermal conductivity was noted in the work of Yoo et al. [12]. Both of these phenomena would be expected to result in degradation of nanofluid thermal conductivity because nanofluid thermal conductivity would be expected to decrease as nanoparticle concentration decreases and as nanoparticle size increases. However, to support such assertions, additional analysis is necessary.

Future work

In future efforts to confirm stated hypothesizes, it is proposed that measurements of the temporal evolution of nanofluid thermal conductivity be conducted once again and combined with evaluations of other important fluid parameters. Specifically, nanoparticle size distributions will be evaluated at appropriate time intervals during the execution of the experiment to evaluate assertions that the average nanoparticle size increases during the execution of the experiment. Nanofluid pH will also be evaluated at certain time intervals due to the potential for this parameter to affect nanofluid colloidal stability. Pictorial data of the nanofluid appearance over time will also be acquired to provide a qualitative demonstration of the development of a nanoparticles concentration gradient in the fluid volume. Such efforts will allow a more complete analysis of the temporal evolution of nanofluid thermal conductivity and mechanisms controlling this phenomenon.

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APPENDIX

The methodology implemented by the KD2 Pro Thermal Properties Analyzer (Decagon Devices) to measure fluids' thermal properties is detailed in the operator's manual supplied with this device [13]. The basis for this system's measurements is the Carslaw-Jaeger model [18], which describes heat conduction in solids. It should be noted that while the model implemented describes the conduction of heat in solids it has been expanded to allow description of this phenomenon in liquids through the assumption that the liquid is stagnant. Support for this expansion is detailed in the work of Cobos [15].

The Carslaw-Jaeger model [18] assumes an instantaneous application of heat to an infinitesimally thin, zero mass source which is located in an infinite medium. This model is represented by Equation A, where a medium's thermal conductivity (k) and thermal diffusivity (D), are related to the temperature difference (ΔT) between the heat source and surrounding medium at a distance (r) from the source of a quantity of heat (Q) a certain time (t) after the heat has been applied.

$$\Delta T = \frac{Q}{4\pi kt} \text{EXP} \left(\frac{-r^2}{4Dt} \right) \quad (\text{A})$$

While this model does serve as the basis for the measurements of thermal conductivity in a given medium, the device utilizes an adaptation of this model which allows the modeling of an identical system in which heat is applied over a finite period of time [13].

This model is presented by Equations B and C, where the thermal conductivity of a material (k) and thermal diffusivity (D), are related to the temperature difference (ΔT) between the heat source and surrounding medium at a distance (r) from the heat source and a certain time (t) after the heat has been applied. It should be noted, that in these models, q represents the rate of heat dissipation, t_1 the time over which the fluid is heated, and Ei denotes the exponential integral that is specified in the work of Abramowitz and Stegun [19].

$$\Delta T = -\frac{q}{4\pi k} \text{EXP}\left(\frac{-r^2}{4Dt}\right) \quad 0 < t \leq t_1 \quad (\text{B})$$

$$\Delta T = -\frac{q}{4\pi k} \left[-Ei\left(\frac{-r^2}{4Dt}\right) + Ei\left(\frac{-r^2}{4D(t-t_1)}\right) \right] \quad t_1 < t \quad (\text{C})$$

In the work of Cobos [15], and the operator's manual accompanying the measurement device [13], a description of the physical implementation of these relationships is provided. Cobos [15] notes that the device measures the temperature response of a given medium to the transient application of heat to a system probe. According to the operator's manual provided by Decagon Devices [13][12], these measurements are compared to the model presented in Equations B and C through the implementation of an algorithm developed by Marquardt [20]. This algorithm allows comparison of the measured temperature response of the system to model developed to ensure this

adequately describes these physical measurements. This comparison provides a quantitative measure of this comparison in the form of a calculated residual value (r^2).

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